

A Critical Temperature Window for Coal Hydropyrolysis

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Abstract

Pyrolysis of coals in the presence of hydrogen is known to enhance liquid yields, but this enhancement is often accompanied by increases in methane make. In many instances increased methane yields are detrimental because of the amount of hydrogen consumed to make methane. This paper will discuss the discovery of a critical temperature threshold for coal hydropyrolysis, below which little methane is formed, and above which significant methane is produced. A simple procedure is described to determine the critical temperature, which is different for each coal and pressure regime used.

INTRODUCTION

Coal has an atomic hydrogen to carbon ratio less than unity. To make desirable liquids, with atomic H/C ratios of 1.5 to 2, hydrogen must be added or carbon removed. The latter approach involves pyrolysis of the coal to produce liquids, gases and a carbonaceous residue called coke or char depending on whether the coal became plastic during the pyrolysis. In the past many researchers have tried to increase the yield of liquids by performing the pyrolysis in the presence of hydrogen under pressure⁽¹⁻⁶⁾. In general, these researchers obtained increased liquid and hydrocarbon gas (C_1 to C_3) yields from such hydropyrolysis methods relative to pyrolysis under inert atmospheres. These increases came at the expense of significant hydrogen uptake, and the hydrogen reported mainly to the hydrocarbon gases.

In our studies of coal hydropyrolysis, we confirmed the yield increase trends previously observed. While examining the effect of temperature on the hydro-pyrolysis reaction we found that a temperature threshold exists, below which increased liquid yields are obtained without production of large quantities of hydrocarbon gases. Details of this finding are described in this paper.

EXPERIMENTAL

Hydropyrolysis reactions were carried out in a fixed bed apparatus, a schematic diagram of which is shown in Figure 1. The 620 cc reactor was capable of sustaining pressures of up to 13.3 MPa, and was heated by means of a fluidized sand bath, which could be raised and lowered hydraulically. In a typical experiment, about 400g of coal was charged into the hopper above the reactor and pressurized with either nitrogen or hydrogen. The reactor was placed in the fluidized sand bath and heated at a rate of about 4°C/min, with preheated nitrogen or hydrogen flowing through it at a rate of about 0.4 SCFM at a predetermined reaction pressure. At an appropriate temperature, coal from the hopper was charged to the reactor by opening a butterfly valve, while the heating rate was adjusted to about 2°C/min. Volatile products were carried out of the reactor by the flowing gas into a high pressure knock out vessel. After reducing gas pressure to 1 atm it was passed through a cooled low pressure knockout vessel then into a wet test meter. Gas samples were taken every 10 minutes and analyzed on a Carle GC. At the end of the experiment, the sand bath was lowered, the reactor cooled, and liquid and char products were collected. Figure 2 shows typical temperature profiles for both the sand bath and reactor during constant temperature coal pyrolysis under nitrogen. Reactor

temperature drops as coal is added, but rapidly recovers to the temperature of the sand bath.

Determination of the critical temperature threshold was accomplished by following the above procedure using hydrogen gas at a flow rate of 0.4 SCFM. Coals were added to the reactor at a temperature of 360°C and heating was continued to 525°C. In Figure 3 the temperatures of the sand bath and the reactor are plotted for a typical experiment. We define the critical temperature as the point where the exotherm begins.

RESULTS AND DISCUSSION

Pyrolysis under hydrogen is known to produce higher yields of liquid and hydrocarbon gas products relative to pyrolysis under nitrogen. This was verified using a subbituminous coal following the above procedure, at a pressure of 7MPa and a constant temperature of 525°C. In the hydrogen case, an exotherm was noted after 3 minutes. Figure 4 shows the evolution of gases on a cumulative basis from the coal during pyrolysis under nitrogen at 525°C, and Figure 5 shows cumulative gas evolution and hydrogen consumption rate for the reaction under 7 MPa of hydrogen at 525°C. In the nitrogen case, liquid yield was 10 wt% (dry coal basis), while under hydrogen, liquid yield was 14 wt%. Notably different were the methane yields in nitrogen and hydrogen, 2 wt% for the former and almost 15 wt% for the latter. From Figure 5 it can be seen that hydrogen consumption rate parallels methane evolution, which implies that the increased methane yield is due to the some form of hydrogasification of the coal or char.

To better understand this observation, the hydropyrolysis was carried out under the programmed temperature conditions described above. Figure 3 shows the temperature profile. Clearly an exotherm occurs at about 45 minutes residence time (temperature of about 465°C). Figure 6 shows the gas evolution for this reaction from which it can be seen that significant methane evolution occurs at about the same time as the exotherm. We define the temperature at which the exotherm appears as a critical temperature threshold.

As indicated in Table 1, the critical temperature threshold appears to be dependent upon hydrogen pressure, decreasing with increasing pressure. Once again the yield of oil is relatively constant, but the methane make is directly related to hydrogen pressure.

Table 1

Onset of Exotherm and Methane Yield Related to Hydrogen Pressure

(370-525°C; 0.4 SCFM)

<u>HYDROGEN PRESSURE, MPa</u>	<u>1.4</u>	<u>7.0</u>	<u>9.2</u>
EXOTHERM, °C	488	465	437
<u>YIELDS, WT% COAL</u>			
METHANE	7.0	11.9	23.0
C ₂ + C ₃	2.2	2.4	2.2
OILS	12.8	14.7	14.8
CHAR	55.3	44.6	38.0
HYDROGEN CONSUMPTION (wt% coal)	2.32	3.76	5.14

The effect of the exotherm on product yields and hydrogen consumption was determined by carrying out the hydropyrolysis in such a way that the reaction temperature never exceeded the critical temperature, which for this coal at these reaction conditions was 465°C. Figure 7 displays the thermal history of this experiment. Several minutes before the critical temperature was reached, the sand bath was lowered, thus assuring that the maximum temperature did not exceed the critical temperature. It is apparent from the figure that the exotherm was completely eliminated in this experiment. Figure 8 shows the gas evolution with time, and it can be seen that methane make is low and in the same range as that for pyrolysis under nitrogen. Table 2 shows a direct comparison of the yield patterns from the hydropyrolysis conducted below and above the critical temperature.

Table 2
Higher Temperature Increases Conversion to Gas Not Oil.
(0.4 SCFM; 7MPa H₂)

<u>YIELDS (WT% COAL)</u>	<u>372-465°C</u> <u>35 MIN</u>	<u>371-525°C</u> <u>85 MIN</u>
METHANE	1.4	11.2
C ₂ + C ₃	1.2	2.4
OILS	14.3	14.7
CHAR	64.5	44.6
HYDROGEN CONSUMPTION (wt% coal)	0.6	3.7

It is obvious from these data that higher pyrolysis temperatures do increase overall conversions, but it is striking that oil yields change very little. Most of the conversion increase is manifested in the methane make. The most significant finding from these data is that hydrogen consumption increases six fold at the higher temperature without adding to the liquid yield. The additional hydrogen appears to be consumed in producing methane.

All of the data discussed to this point was taken on a subbituminous coal. To determine whether the effect is important for coals of different rank, the hydropyrolysis was carried out on a bituminous coal. The data for these experiments are summarized in Table 3 and compared to those from the subbituminous coal. In these experiments the bituminous coal was impregnated with a concentrated potassium hydroxide solution to aid in preventing agglomeration. The treated coal contained 8.44 wt% acid soluble potassium. The critical temperature for this coal was determined in separate experiments to be 474°C and the hydropyrolysis was carried out below the temperature. It can be seen from Table 3 that liquid yield from the bituminous coal increased by about twofold under these hydropyrolysis conditions, while the hydrocarbon gas make is only slightly higher than that produced under nitrogen. Much more work on other coals must be done before a firm conclusion can be made regarding generality, but the data gathered thus far support this as a tentative conclusion.

Virtually nothing is known with certainty regarding the mechanism or mechanisms involved in this phenomenon. One obvious mechanism for methane formation is hydrodealkylation of side chains. If dealkylation is a major pathway, it should be possible to observe differences in the infrared spectra of hydropyrolysis chars made above and below the critical temperature. Figure 9a is a Fourier Transform IR

Table 3

Critical Temperature Threshold May be General

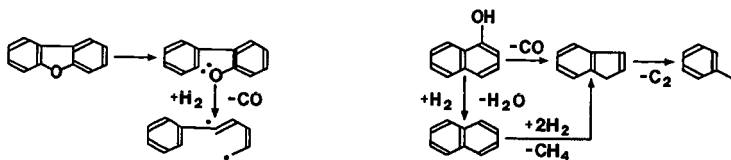
	<u>SUBBITUMINOUS</u>	<u>BITUMINOUS*</u>
CRITICAL TEMP., °C	465	474
LIQUID YIELD (WT% DAF) IN		
H_2	15.5	18.7
N_2 (525°C)	11.3	9.7
$\text{C}_1\text{-C}_3$ (WT% DAF) IN		
H_2	2.8	6.4
N_2 (525°C)	5.6	5.0
CHAR (WT% DAF) IN		
H_2	61.5	58.4
N_2 (525°C)	66.4	68.1

* KOH treated

spectrum of the char from the hydropyrolysis reaction which produced 11.2 wt% methane (Table 2), and Figure 9b is the difference spectrum between Figure 9a and that of the spectrum of the char from the hydropyrolysis reaction which made 1.4 wt% methane (Table 2). Figure 9b does not indicate significant differences between the two chars. This appears to be inconsistent with a hydrodealkylation hypothesis.

Elemental analyses of the chars show that oxygen remaining in the chars decrease as more methane is made. These data are displayed in Figure 10, as methane yield plotted against atomic O/C ratio, and may indicate that carbon-oxygen bonds are the sites most readily attacked by hydrogen.

One set of mechanisms which appear to be consistent with the observations discussed above are those proposed by Graber and Hutterling⁽⁷⁾. They subjected many aromatic, alkylaromatic and heteroatom-containing aromatic model compounds to hydro-pyrolysis at temperatures varying between 600-1000°C. Among their conclusions, they found that oxygen in aromatic rings and hydroxyl groups of phenol and naphthol strongly enhance the methane yield, and that decarbonylation was a key step for both types of oxygen compounds:



Nitrogen containing aromatic systems also showed a propensity to form methane under their conditions. Analyses of the chars described above showed an inverse dependence of methane yield to the atomic N/C ratio.

CONCLUSIONS

A critical temperature threshold exists for coal hydrolysis, above which methane forms rapidly with a concomitant increase in hydrogen consumption. Liquid yields are not increased above the critical temperature. The critical temperature threshold may be a general phenomenon, and depends upon coal, i.e., bituminous or subbituminous coal, hydrogen partial pressure and hydrogen treatment rate. The chemistry and mechanisms involved in the effect are not well understood. Preliminary results indicate that dealylation may not be a major route to methane formation, and that the reactions to produce methane take place at heteroatom sites, particularly oxygen and nitrogen, in the char.

This work suggests that controlling the temperature of the hydrolysis below that of the critical temperature is an important means to improve the utilization of hydrogen, thus improving the efficiency of any hydrolysis process.

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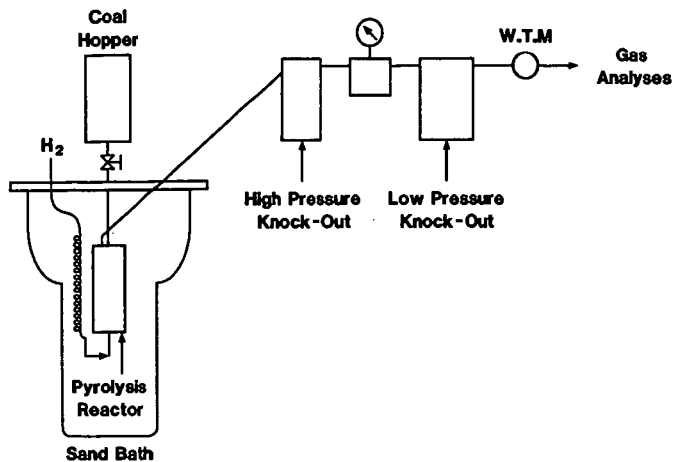


Fig. 1. Fixed Bed Hydropyrolysis Apparatus

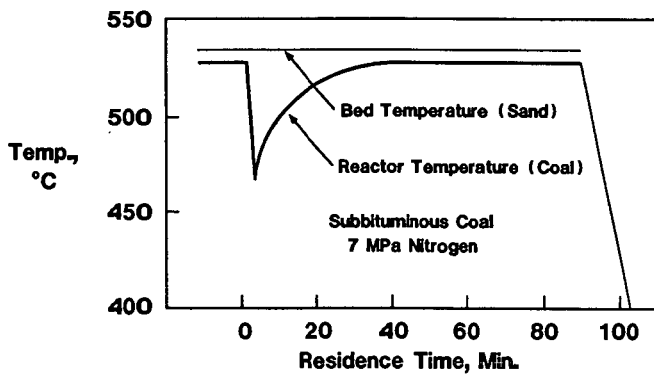


Fig. 2. Typical Thermal History of Coal Under Nitrogen

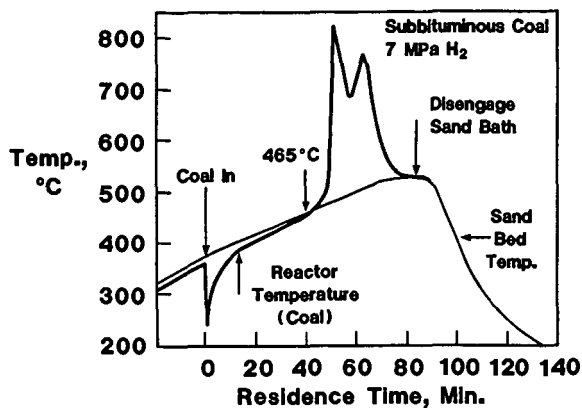


Fig. 3. Programmed Hydropyrolysis Heatup Exhibits Exotherm

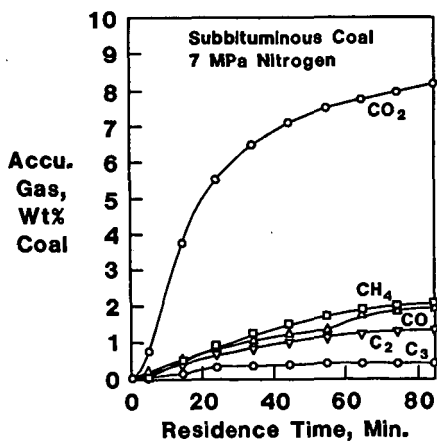


Fig. 4. Low CH₄ Yield From Nitrogen Pyrolysis at 525°C

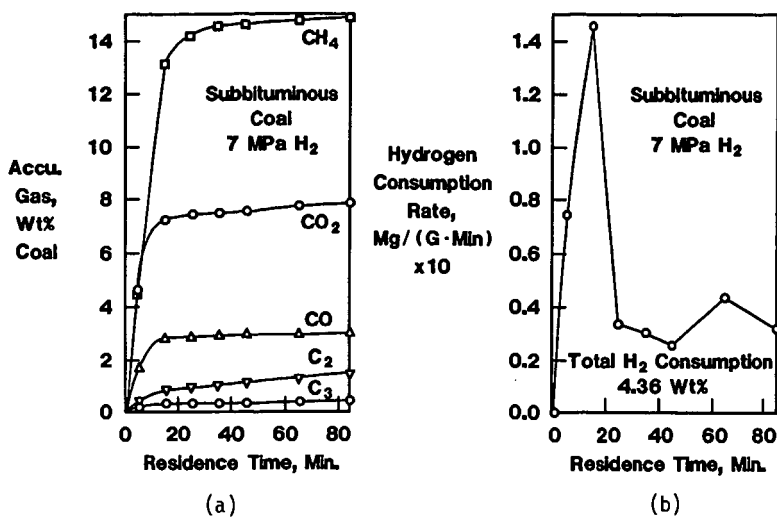


Fig. 5. (a) Gas Make and (b) Hydrogen Consumption Rate for Hydropyrolysis at 525°C

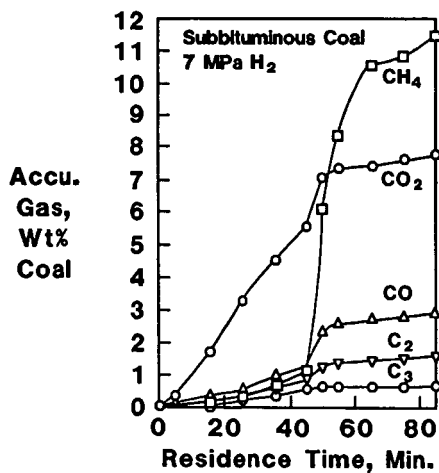


Fig. 6. Increased CH₄ Evolution with Onset of Exotherm

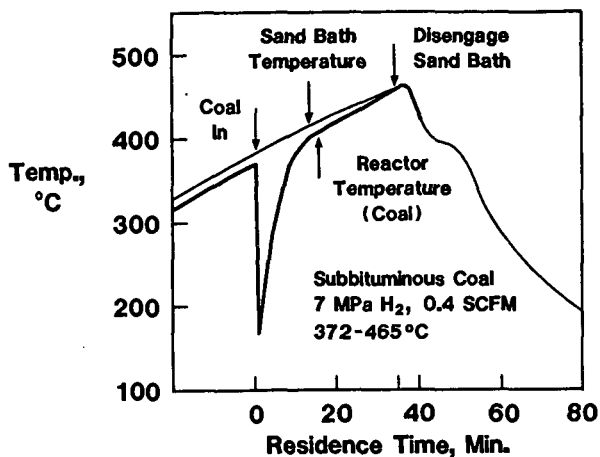


Fig. 7. Controlled Heatup to Below 465°C Eliminates Exotherm

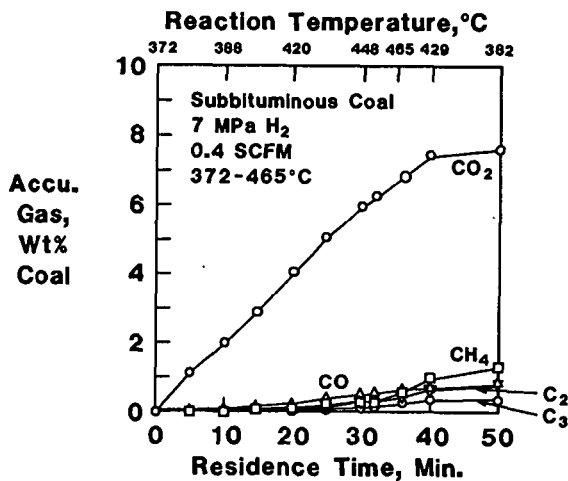


Fig. 8. Rapid Methane Formation is Eliminated

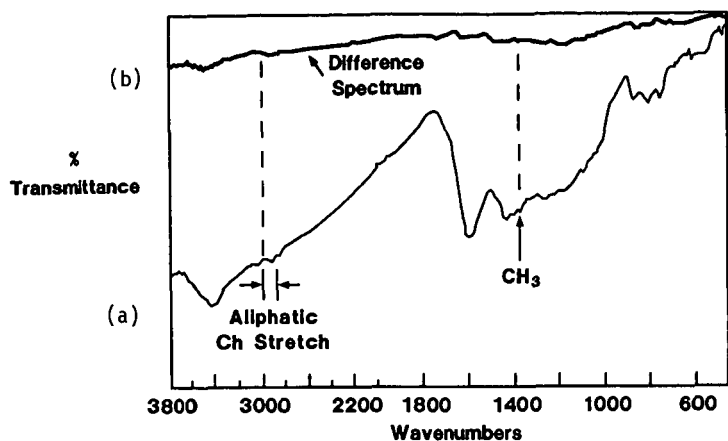


Fig. 9. (a) FTIR Spectrum of Char (11.2 wt.% CH₄); (b) Difference Spectrum of Chars (11.2 wt.% CH₄ and 1.4 wt.% CH₄)

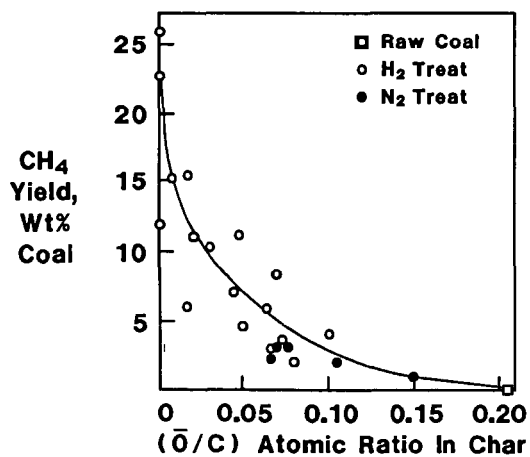


Fig. 10. Methane Yields Inversely Proportional to Oxygen in Char